CLAIMS

We claim:

ART 34 ANDT (all claim pages)

1

1. A compound having the structure:

$$R_{11}$$
 R_{10}
 R_{10}
 R_{11}
 R_{10}
 R_{11}
 R

wherein R_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R₁ and R₂, when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

R₁ and R₃, when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R₄ is hydrogen or halogen;

R₅ is hydrogen, an oxygen protecting group or a prodrug;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

 R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

WO 03/076424

wherein R₁₂ and R₁₃ are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R₁₂ and R₁₃, taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R₁₂ and R₁₃ are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or aliphatic, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; and

pharmaceutically acceptable derivatives thereof.

2. The compound of claim 1, where the following groups do not occur simultaneously as defined:

X is oxygen,

R₁ is methyl,

R₂ and R₃ are each hydrogen,

R4 is hydrogen,

R₅ is hydrogen, lower alkyl or lower alkanoyl,

R₆ is OR', where R' is hydrogen, lower alkyl or lower alkanoyl with S-configuration,

R₇ is hydrogen,

Y and Z together represent -CHR₁₇-CHR₁₈-or -CR₁₇=CR₁₈-, wherein R_{17} and R_{18} are independently hydrogen, or when Y and Z are - CHR₁₇-CHR₁₈, R_{17} and R_{18} taken together are -O-;

 R_8 is hydrogen or OR', where R' is hydrogen, lower alkyl or lower alkanoyl,

 R_9 is OR', where R' is hydrogen, lower alkyl or lower alkanoyl, R_{10} is OR", where R" is hydrogen, lower alkyl or lower alkanoyl; and R^{11} is hydrogen.

3. The compound of claim 1, wherein:

 \mathbf{R}_1 is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

 \mathbf{R}_5 is hydrogen or a protecting group;

 \mathbf{R}_{6} is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R₈ is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR₁₂, or NR₁₂R₁₃;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2$ - R_{14} , or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2$ - R_{14} ;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

 \mathbf{R}_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R₁₇ and R₁₈ is independently hydrogen or lower alkyl, or R₁₇ and R₁₈ taken together is -O-, $-CH_{2}$ - or $-NR_{19}$ -, wherein R₁₉ is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; and

pharmaceutically acceptable derivatives thereof.

- 4. The compound of claim 3, where X is oxygen and n is 1.
- 5. The compound of claim 3, where R_4 is halogen.
- 6. The compound of claim 3, where R_4 is fluorine.
- 7. The compound of claim 3, where Y and Z together represent-CH=CH-
- 8. The compound of claim 3, where Y and Z together represent trans -CH=CH-.
- 9. The compound of claim 3, wherein R_1 and R_2 are each methyl and R_3 is hydrogen and the compound has the structure:

$$R_{11}$$
 R_{10}
 R

wherein R₄-R₁₁, n, X, Y and Z are as defined in claim 3.

- 10. The compound of claim 9, wherein X is oxygen and n is 1.
- 11. The compound of claim 9, wherein R_4 is halogen.

- 12. The compound of claim 9, wherein Y and Z together represent -CH=CH.
- 13. The compound of claim 9, wherein X is oxygen, n is 1, R₄ is halogen and Y and Z together represent -CH=CH-.
- 14. The compound of claim 12 or 13 wherein -CH=CH- is trans.
- 15. The compound of claim 3, wherein R_9 is $NR_{12}R_{13}$ and the compound has the structure:

$$R_{12}$$
 R_{13}
 R_{12}
 R_{13}
 R_{14}
 R_{15}
 R

wherein R₁-R₁₂, n, X, Y and Z are as defined in claim 3, or

 R_{13} and R_8 may, when taken together, form a cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydrogen, alkyloxy, amino, alkylamino, aminoalkyl, and halogen.

- 16. The compound of claim 15, wherein X is oxygen and n is 1.
- 17. The compound of claim 15, wherein R₄ is halogen.
- 18. The compound of claim 15, wherein Y and Z together represent -CH=CH-.
- 19. The compound of claim 15, wherein R_1 and R_2 are each methyl and R_3 is hydrogen.

- 20. The compound of claim 15, wherein X is oxygen, n is 1, R_1 and R_2 are each methyl, R_3 is hydrogen, R_4 is halogen, and Y and Z together represent -CH=CH-.
- 21. The compound of claim 18 or 20, wherein -CH=CH- is trans.
- 22. A compound having the structure:

23. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

25. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

26. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

28. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

29. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

31. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

32. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

34. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

35. A compound having the structure:

and pharmaceutically acceptable derivatives thereof.

37. A pharmaceutical composition comprising: a compound having the structure:

$$R_{11}$$
 R_{10}
 R_{10}
 R_{11}
 R_{2}
 R_{3}
 R_{2}
 R_{3}
 R_{2}
 R_{3}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{7}
 R_{6}
 R_{7}
 R_{6}

wherein \mathbf{R}_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

 R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R₁ and R₂, when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

 R_1 and R_3 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R₄ is hydrogen or halogen;

R₅ is hydrogen, an oxygen protecting group or a prodrug;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

 R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R₁₇ and R₁₈ is independently hydrogen or aliphatic, or R₁₇ and R₁₈ taken together is -O-, $-CH_2$ - or $-NR_{19}$ -, wherein R₁₉ is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and

a pharmaceutically acceptable carrier.

- 38. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit NF-kB activation.
- 39. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit AP-1 activation.
- 40. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit a protein kinase.
- 41. The pharmaceutical composition of claim 39, wherein the protein kinase is MEKK1, MEK1, VEGFr or PDGFr.
- 42. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit proliferation of cancerous cells and angiogenesis on solid tumors.
- 43. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to have an anti-inflammatory effect.
- 44. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to treat psoriasis.
- 45. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to reduce skin photodamage.
- 46. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to prevent restenosis.
- 47. The pharmaceutical composition of claim 37, where:

 \mathbf{R}_{1} is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R4 is hydrogen or halogen;

R₅ is hydrogen or a protecting group;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R₈ is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR₁₂, or NR₁₂R₁₃;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or lower alkyl, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond.

- 48. The pharmaceutical composition of claim 47, where X is oxygen and n is 1.
- 49. The pharmaceutical composition of claim 47, where R₄ is halogen.
- 50. The pharmaceutical composition of claim 49, where R₄ is fluorine.
- 51. The pharmaceutical composition of claim 47, where Y and Z together represent CH=CH-.
- 52. The pharmaceutical composition of claim 51, wherein -CH=CH- is trans.

53. The pharmaceutical composition of claim 47, wherein R_1 and R_2 are each methyl and R_3 is hydrogen and the compound has the structure:

wherein R₄-R₁₁, n, X, Y and Z are as defined in claim 46.

- 54. The pharmaceutical composition of claim 53, wherein X is oxygen and n is 1.
- 55. The pharmaceutical composition of claim 53, wherein R₄ is halogen.
- 56. The pharmaceutical composition of claim 53, wherein Y and Z together represent CH=CH-.
- 57. The pharmaceutical composition of claim 53, wherein X is oxygen, n is 1, R₄ is halogen, and Y and Z together represent -CH=CH-.
- 58. The pharmaceutical composition of claim 56 or 57, wherein -CH=CH- is trans.
- 59. The pharmaceutical composition of claim 47, wherein R₉ is NR₁₂R₁₃ and the compound has the structure:

wherein R₁-R₁₃, n, X, Y and Z are as defined in claim 46, or

R₁₃ and R₈ may, when taken together, form a cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydrogen, alkyloxy, amino, alkylamino, aminoalkyl, and halogen.

- 60. The pharmaceutical composition of claim 59, wherein X is oxygen and n is 1.
- 61. The pharmaceutical composition of claim 59, wherein R₄ is halogen.
- 62. The pharmaceutical composition of claim 59, wherein Y and Z together represent CH=CH-.
- 63. The pharmaceutical composition of claim 59, wherein R_1 and R_2 are each methyl and R_3 is hydrogen.
- 64. The pharmaceutical composition of claim 59 wherein X is oxygen, n is 1, R_1 and R_2 are each methyl, R_3 is hydrogen, R_4 is halogen, and Y and Z together represent -CH=CH-.
- 65. The pharmaceutical composition of claim 63 or 64 wherein -CH=CH- is trans.
- 66. A pharmaceutical composition comprising: a compound having the structure:

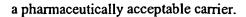
and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

67. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

68. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and



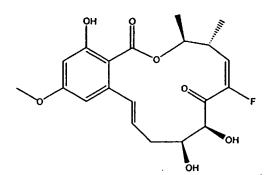
69. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

70. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

71. A pharmaceutical composition comprising: a compound having the structure:



and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

72. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

73. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and

a pharmaceutically acceptable carrier.

74. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

75. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

76. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

77. A pharmaceutical composition comprising:
a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

78. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

79. A pharmaceutical composition comprising:

a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

80. A pharmaceutical composition comprising: a compound having the structure:

and pharmaceutically acceptable derivatives thereof; and a pharmaceutically acceptable carrier.

81. A topical pharmaceutical composition for preventing or treating UVB-induced photodamage comprising:

$$\begin{array}{c|c}
R_{11} & O & R_{1} & R_{3} & R_{2} \\
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R_{11} & O & R_{1} & R_{3} & R_{2} \\
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R_{11} & O & R_{1} & R_{3} & R_{2} \\
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R_{15} & O & R_{3} & R_{3} & R_{3} \\
\hline
R_{15} & O & R_{3} & R_{3} & R_{3} \\
\hline
R_{15} & O & R_{3} & R_{3} & R_{3} \\
\hline
R_{15} & O & R_{3} & R_{3} & R_{3} & R_{3} \\
\hline
R_{15} & O & R_{3} & R_{3} & R_{3} \\
\hline
R_{15} & O & R_{3} & R_{3} & R_{3} \\
\hline
R$$

wherein R_1 is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

R₅ is hydrogen or a protecting group;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R₈ is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR₁₂, or NR₁₂R₁₃;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or

WO 03/076424

more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 -R₁₄ together are N₃ or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=0)NHR_{15}$ $-(C=0)OR_{15}$, or $-(C=0)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or lower alkyl, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and

a pharmaceutically acceptable carrier;

wherein the compound is present in an amount effective to prevent or treat UVB-induced photodamage.

- 82. The pharmaceutical composition of claim 81, further comprising a cosmetic ingredient.
- 83. The pharmaceutical composition of claim 82, wherein the cosmetic ingredient is a sunscreen.

84. A method for treating an inflammatory and/or autoimmune disorder or a disorder resulting from increased angiogenesis and/or cell proliferation comprising:

administering to a subject in need thereof a therapeutically effective amount of a compound having the structure:

$$R_{11}$$

$$R_{10}$$

$$R_{10}$$

$$R_{10}$$

$$R_{11}$$

$$R_{10}$$

$$R_{11}$$

$$R$$

wherein R_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

 $\mathbf{R_2}$ and $\mathbf{R_3}$ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R₁ and R₂, when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

R₁ and R₃, when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R₄ is hydrogen or halogen;

R₅ is hydrogen, an oxygen protecting group or a prodrug;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

 R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

WO 03/076424

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=0)NHR_{15}$ $-(C=0)OR_{15}$, or $-(C=0)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or aliphatic, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and

a pharmaceutically acceptable carrier or diluent.

- 85. The method of claim 84, wherein the method is for treating a disorder selected from the group consisting of rheumatoid arthritis, psoriasis, asthma, cancer, sepsis, inflammatory bowel disease, atopic dermatitis, Crohn's disease, and autoimmune disorders.
- 86. The method of claim 84, wherein the method is for treating rheumatoid arthritis.
- 87. The method of claim 84, wherein the method is for treating psoriasis.
- 88. The method of claim 84, wherein the method is for treating asthma.
- 89. The method of claim 84, wherein:

 $\mathbf{R}_{\mathbf{l}}$ is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

R₅ is hydrogen or a protecting group;

 \mathbf{R}_{6} is hydrogen, hydroxyl, or protected hydroxyl;

WO 03/076424

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R₈ is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR₁₂, or NR₁₂R₁₃;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen:

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R₁₇ and R₁₈ is independently hydrogen or lower alkyl, or R₁₇ and R₁₈ taken together is -O-, $-CH_2$ - or $-NR_{19}$ -, wherein R₁₉ is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond.

- 90. The method of claim 89, wherein in the compound X is oxygen and n is 1.
- 91. The method of claim 89, wherein in the compound R₄ is halogen.
- 92. The method of claim 89 is wherein in the compound R₄ is fluorine.
- 93. The method of claim 89, wherein in the compound Y and Z together represent-CH=CH-
- 94. The method of claim 93, wherein in the compound Y and Z together represent trans -CH=CH-.
- 95. The method of claim 89, comprising administering a compound wherein R_1 and R_2 are each methyl and R_3 is hydrogen and the compound has the structure:

$$R_{11}$$
 R_{10}
 R

wherein R₄-R₁₁, n, X, Y and Z are as defined in claim 88.

- 96. The method of claim 95, wherein in the compound X is oxygen and n is 1.
- 97. The method of claim 95, wherein in the compound R₄ is halogen.

- 98. The method of claim 95, wherein in the compound Y and Z together represent -CH=CH.
- 99. The method of claim 95, wherein in the compound X is oxygen, n is 1, R₄ is halogen and Y and Z together represent -CH=CH-.
- 100. The method of claim 98 or 99 wherein in the compound -CH=CH- is trans.
- 101. The method of claim 89, comprising administering a compound wherein R_6 is $NR_{11}R_{12}$ and the compound has the structure:

wherein R₁-R₁₃, n, X, Y and Z are as defined in cliam 87, or

R₁₃ and R₈ may, when taken together, for a cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydrogen, alkyloxy, amino, alkylamino, aminoalkyl, and halogen.

- 102. The method of claim 101, wherein in the compound X is oxygen and n is 1.
- 103. The method of claim 101, wherein in the compound R₄ is halogen.
- 104. The method of claim 101, wherein in the compound Y and Z together represent -CH=CH-.
- 105. The method of claim 101, wherein in the compound R_1 and R_2 are each methyl and R_3 is hydrogen.

- 106. The method of claim 101, wherein in the compound X is oxygen, n is 1, R_1 and R_2 are each methyl, R_3 is hydrogen, R_4 is halogen, and Y and Z together represent -CH=CH-.
- 107. The method of claim 105 or 106, wherein in the compound -CH=CH- is trans.
- 108. The method of claim 84, comprising administering a compound having the structure:

109. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

110. The method of claim 84, comprising administering a compound having the structure:

111. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

112. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

113. The method of claim 84, comprising administering a compound having the structure:

114. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

115. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

116. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

117. The method of claim 84, comprising administering a compound having the structure:

and pharmaceutically acceptable derivatives thereof.

118. The method of claim 84, comprising administering a compound having the structure:

119. A method for providing protection against UVB-induced photodamage to a subject, said method comprising:

Administering to the subject in need thereof a composition comprising a compound having the structure:

$$\begin{array}{c|c}
R_{11} & & & \\
R_{11} & & &$$

wherein R_1 is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

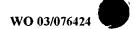
wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

 R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

R₅ is hydrogen or a protecting group;



R₆ is hydrogen, hydroxyl, or protected hydroxyl; n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

 R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2$ - R_{14} , or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2$ - R_{14} ;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or lower alkyl, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and

a pharmaceutically acceptable carrier or diluent.

- 120. The method of claim 119, wherein in the step of administering, the composition is administered topically.
- 121. The method of claim 119, wherein the photodamage is skin wrinkles.
- 122. The method of claim 119, wherein the photodamage is a skin cancer.
- 123. A method for preventing or reducing the rate of restenosis, comprising:

inserting a stent into an obstructed blood vessel, the stent having a generally tubular structure, the surface of the structure being coated with (or otherwise adapted to release) a composition comprising a compound having the structure:

$$\begin{array}{c|c}
R_{11} & & & \\
R_{11} & & & \\
R_{2} & & & \\
R_{3} & & & \\
R_{4} & & & \\
R_{5} & & & \\
R_{7} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{1} & & & \\
R_{3} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{2} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{1} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{2} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{1} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{2} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{2} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{2} & & & \\
\end{array}$$

$$\begin{array}{c|c}
R_{3} & & \\
\end{array}$$

wherein R_1 is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; WO 03/076424

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

R₅ is hydrogen or a protecting group;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R₈ is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR₁₂, or NR₁₂R₁₃;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R₁₀ is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R₁₁ is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH2 or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R_{17} and R_{18} is independently hydrogen or lower alkyl, or R_{17} and R_{18} taken together is -O-, -CH₂- or -NR₁₉-, wherein R_{19} is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and optionally

a pharmaceutically acceptable carrier or diluent;

such that the obstruction is eliminated and the composition is delivered in amounts effective to prevent or reduce the rate of restenosis.

124. A method for expanding the lumen of a body passageway, comprising:

inserting a stent into the passageway, the stent having a generally tubular structure, the surface of the structure being coated with (or otherwise adapted to release) a composition comprising a compound having the structure:

$$\begin{array}{c|c}
R_{11} & R_{10} & R_{11} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{10} & R_{11} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{10} & R_{11} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{12} & R_{13} & R_{13} & R_{12} & R_{13} & R_{12} \\
R_{11} & R_{12} & R_{13} & R_{13} & R_{12} & R_{13} \\
R_{12} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{12} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{13} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{13} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{13} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{13} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{14} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{13} & R_{13} & R_{13} \\
R_{15} & R_{13} & R_{$$

wherein R_1 is hydrogen, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R₂ and R₃ are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched lower alkyl, straight or branched lower heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R₁ and R₂, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R₁ and R₃, when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R₄ is hydrogen or halogen;

R₅ is hydrogen or a protecting group;

R₆ is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R₇, for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

 R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or lower alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

 R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, - $X_1(CH_2)_pX_2-R_{14}$, or is lower alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or - $X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, lower alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

 R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is - (C=O)NHR₁₅ - (C=O)OR₁₅, or - (C=O)R₁₅, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is -SO₂(R_{16}), wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R₈ and R₉ may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

 R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino; R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH₂ or S;

Y is CHR₁₇, O, C=O, CR₁₇ or NR₁₇; and Z is CHR₁₈, O, C=O, CR₁₈ or NR₁₈, wherein each occurrence of R₁₇ and R₁₈ is independently hydrogen or lower alkyl, or R₁₇ and R₁₈ taken together is -O-, $-CH_2$ - or $-NR_{19}$ -, wherein R₁₉ is hydrogen or lower alkyl, and Y and Z may be connected by a single or double bond; pharmaceutically acceptable derivatives thereof; and optionally

a pharmaceutically acceptable carrier or diluent;

- · such that the passageway is expanded.
- 125. The method of claim 124, wherein the lumen of a body passageway is expanded in order to eliminate a biliary, gastrointestinal, esophageal, tracheal/bronchial, urethral and/or vascular obstruction.
- 126. The method of claim 125, wherein the lumen of a body passageway is expanded in order to eliminate a vascular obstruction.